

RECOMBINATION FLUORESCENCE OF ANTHRACENE IN A MAGNETIC FIELD

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The quenching of recombination fluorescence by a magnetic field is discussed. Fluorescence was induced by double injection, of electrons and holes, from liquid electrodes into an anthracene single crystal. The fast and delayed fluorescence components were separated by the use of a pulsed voltage. It is demonstrated that a magnetic field affects only the delayed component, which appears when a high concentration of molecular triplet excitons accumulates in the sample. A model that can account for the effect of a magnetic field on fluorescence is proposed, based on the previously described variation in the lifetime of large-radius Π excitons (charge-transfer type) produced by electron-hole recombination. A novel feature of the model consists in the presence of two electron conduction bands, a narrow band (e_i) and a higher-energy broadband (e). Recombination of the e_i electrons results in the formation of Π excitons, which annihilate nonradiatively. The narrow-band electrons e_i recombine; the production of molecular singlet and triplet excitons results. Injection from the electrodes takes place into the narrow band. Coupling between the bands can be caused by the processes $e_i \rightarrow e$ (through $e_i + h \rightarrow M_T^*$, $M_T^* + M_T^* \rightarrow e + h$) and $e \rightarrow e_i$ (which is a spontaneous process with the rate constant $10^6/\text{sec}$). It is concluded that delayed fluorescence of anthracene results from the recombination of electrons and holes that are produced when molecular triplet excitons are annihilated.

INTRODUCTION

RESULTS obtained by investigators of the negative photoconductive effect observed in anthracene that is placed within a magnetic field have been attributed to field-induced changes in the lifetime of large-radius excitons (the Wannier charge-transfer type).^[1-4] Whenever carriers of both signs are produced by light (occurring in^[4] when molecular triplet excitons recombine), the recombination of holes and electrons leads to the formation of charge-transfer excitons.

High densities of holes and electrons can be injected into anthracene through liquid contacts containing ions that can transfer their charges to the anthracene.^[5] Holes and electrons then also recombine in the interior of the crystal, which now fluoresces. By investigating the behavior of recombination fluorescence in a magnetic field we can determine how the fluorescence is related to charge-transfer excitons, which appear to be individual states that are sensitive to magnetic fields, and to account for the production of these excitons in connection with electron-hole recombination.

In the present work, performed on anthracene single crystals, we have observed the variation of fluorescence intensity in a magnetic field^[1] and we have proceeded to discuss the role of charge-transfer excitons in the new effect.

EXPERIMENT

We achieved double carrier injection into an anthracene single crystal by means of liquid contacts (holes from a solution of anthracene and AlCl_3 in nitromethane, and electrons from a solution of anthracene and Na in tetrahydrofuran) similar to those used in^[5]. Our anthra-

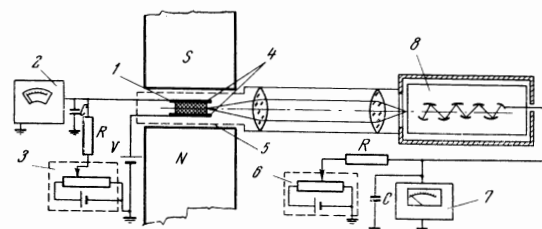


FIG. 1. Scheme for measuring current and fluorescence in a magnetic field following double injection of charges into anthracene. 1—anthracene single crystal, 2—electrometer amplifier (for measuring current through the samples), 3 and 6—compensating circuits, 4—carrier-injecting electrodes (arbitrary representation), 5—light-tight chamber, 7—microvoltmeter (for measuring photomultiplier signals), 8—photomultiplier.

cene single crystals had been grown by the NRC of Canada by means of crystallization from a solution of chromatographic zone-refined anthracene.^[2] The samples, which had been cut along the ab cleavage plane, had thicknesses in the range 0.5–2 mm; the area of contact with an electrode was 0.1 cm^2 .

The anthracene sample was placed in a light-tight chamber mounted in the gap of a permanent magnet. The photomultiplier and all measuring instruments were mounted far enough away from the magnet to avoid stray-field effects. The sensitivity of the photomultiplier changed less than 0.2% when the magnetic field was switched on and light was registered coming from a control source that replaced the sample.

The experimental arrangement is shown in Fig. 1. Measurements were obtained by applying to the electrodes either a constant voltage or pulses having amplitudes up to 1200 V and 10–2000- μsec durations. These

¹We have previously published a brief communication concerning the observed effect of magnetic fields on fluorescence.^[6]

²The authors are very grateful to Professor W. G. Schneider and his collaborators for the anthracene single crystals.

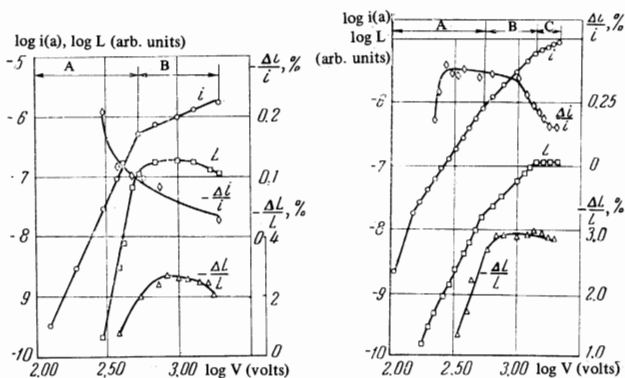


FIG. 2

FIG. 2. Dependence of i , L , $\Delta i/i$, and $\Delta L/L$ on voltage applied to electrodes of a single-crystal 0.07 cm thick in a 3000-Oe field.

FIG. 3. Same as Fig. 3 for a single-crystal 0.2 cm thick in a 3000-Oe field.

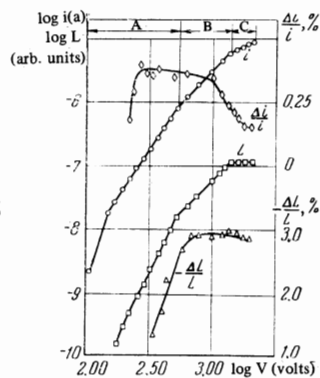


FIG. 3

pulses were furnished by a GIS-2M pulse generator and amplifier. An S1-4 oscillograph was used to register the shapes, amplitudes, and durations of the pulses, along with the current flowing through the sample and fluorescence from the latter. In the registration of mean currents through the sample and the fluorescence the input circuits of the amplifiers were characterized by $RC = 1-2$ sec; in the pulse shape measurements, $RC = 5 \times 10^{-6}$ sec. The high stability and long time constants of the measuring instruments in conjunction with the compensating circuits enabled us to measure relative current changes $\geq 0.03\%$ and relative fluorescence changes $\geq 0.1\%$.

The intensity ratio of the fast (L_f) and delayed (L_S) fluorescence components was determined from the oscillograms. The rise times of these components differed greatly; for the fast component and for the current we had $\tau \approx 10$ μ sec, while for the delayed component $\tau \sim 1000$ μ sec. The component ratio could also be determined from measurements of the mean fluorescence intensity using voltage pulses of different durations.

RESULTS

It was observed that both the current i through the sample and the fluorescence intensity L were affected by switching on the magnetic field. The relative changes $\Delta i/i$ and $\Delta L/L$ increased with the magnetic field, reaching saturation at ≈ 3000 Oe.^[6] Figures 2 and 3 show the dependences on applied voltage that were exhibited by the current i , the fluorescence intensity L , and the maximal ratios $\Delta i/i$ and $\Delta L/L$ in a magnetic field. The curves in Figs. 2 and 3 pertain to crystals of different thicknesses. The values of $\Delta i/i$ and $\Delta L/L$ were not affected by reversal of the magnetic field.

At low voltages the current flowing through the crystal is represented by $i \sim V^n$ and the fluorescence increases very steeply with V (in Fig. 2: for fields to 600 V, $n = 5$ and $L \sim V^{12}$). The respective powers of V representing i and L varied among the different crystals but remained high. For $V > 600$ V (Fig. 2) the current-voltage relation becomes linear. In thick crystals ($l = 2$ mm) an ohmic region appeared at very high volt-

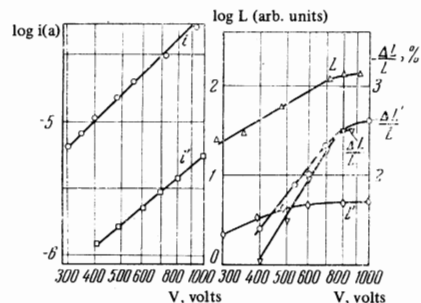


FIG. 4. Dependence of i , L , and $\Delta L/L$ on pulse amplitude; i' , L' , and $\Delta L/L$ designates curves obtained at constant voltages. Crystal thickness 0.1 cm; magnetic field 3000 Oe.

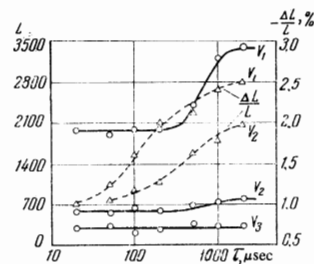


FIG. 5. Dependence of L (photomultiplier output in mV) and $\Delta L/L$ on pulse duration for different voltages: $V_1 = 870$ V, $V_2 = 500$ V, and $V_3 = 300$ V.

ages (>2000 V), as well as a region where $i \sim V^2$ (Fig. 3).

By using a pulsed voltage we established conditions in which no charge was bound in traps of the crystal bulk.^[7] When the pulse duration τ considerably exceeds the time required to populate traps the current is governed by the space charge of free carriers. The measurements showed that when $\tau/T < 10^{-2}$ (where τ/T is the duty factor and T is the spacing of the pulses) the mean current \bar{i} and the mean intensity \bar{L} increase linearly with τ/T . Figure 4 shows peaks of i and L determined from \bar{i} , \bar{L} , and the duty factor as functions of the pulse amplitude. The lower curves provide comparison (i' and L') at constant voltages. It appears that when traps no longer play a part i and L are augmented by about one order of magnitude, although $\Delta i/i$ and $\Delta L/L$ remain unchanged.

We can expect that the delayed fluorescence component will not be present in the short-pulse case. This component depends on the recombination of triplet excitons and its rise time depends on the lifetime $\tau_T \approx 10^{-3}$ sec^[5] of the latter. The delayed component L_S should be present when $\tau > \tau_T$.^[5] Thus at any given voltage the peak values of L will depend on τ . Figure 5 shows the peaks of L plotted as functions of τ at three different voltages: 870, 500, and 300 V. The curve for 870 V (V_1) shows a distinct step; the height ratio between long and short pulses is here $1.7:1 = (L_f + L_S)/L_f$, which corresponds to the already known ratio $L_S/L_f = 0.65 \pm 0.1$.^[5] The step is less pronounced at 500 V (V_2) and does not appear at 300 V (V_3). It follows that when $V < 870$ volts the concentration of triplets generated through hole-electron recombination is insufficient to ensure their total participation in the processes determining delayed fluorescence; recombination processes do not account for the disappearance of all triplet excitons.

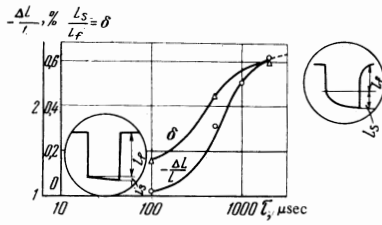


FIG. 6. Dependence of $\delta = L_S/L_f$ and $\Delta L/L$ on pulse duration τ . $V = 870$ V, $H = 3000$ Oe, $l = 0.1$ cm. In the circles on the left and right are shown the fluorescence pulse shapes associated with short ($\tau = 0.1$ msec) and long ($\tau = 2$ msec) square pulses, respectively, applied to the crystal. The slow rise of fluorescence in the right-hand pulse resulted from the delayed component L_S .

Figure 5 also shows the variation of $\Delta L/L$ in a magnetic field at 870 and 500 V; this is characterized by the same values of τ as for the delayed component. The delayed component, which increases like $|\Delta L/L|$ with the pulse amplitude, was also observed directly in oscillograms of fluorescence pulses. Figure 6 shows the dependence of $\delta = L_S/L_f$ and $\Delta L/L$ on pulse duration τ at 870 V and $f = 2.7$ Hz; this was also plotted from the oscillograms. The same figure shows the shapes of fluorescence pulses for $\tau_1 = 2$ μ sec and $\tau_2 = 100$ μ sec. Figures 5 and 6 demonstrate that L is sensitive to a magnetic field only when the delayed component is present.

Figure 7 shows the variation of $\Delta i/i$ in a magnetic field as a function of pulse height for two pulse durations. Figure 8 shows the dependence of $\Delta i/i$ on pulse duration τ at a single frequency for two voltages. These results prove that the current changes in a magnetic field, like the variations in the fluorescence, require the presence of delayed fluorescence and thus the presence of molecular triplet excitons.

DISCUSSION OF RESULTS

1. Current-voltage characteristics for doubly-injected currents. The current curves in Figs. 2 and 3 exhibit a steep rise region (A) ($i \sim V^n$, $n > 2$), a quadratic region (B) ($n = 2$), and a linear region (C) ($n = 1$). These curves are characterized by the fact that the three different regions do not appear to the same extent in each crystal, as can be understood from the following considerations. At low voltages the current through the crystal is governed by the space charge, and in the presence of traps its rise depends on voltage as $i \sim V^n$,^[8] with $n > 2$; the exponent depends on the trap

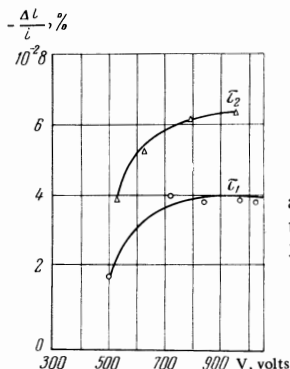


FIG. 7. Dependence of $\Delta i/i$ on pulse amplitude for two different pulse durations: $\tau_1 = 0.1$ msec, $\tau_2 = 1.4$ msec, $H = 3000$ Oe, $l = 0.2$ cm.

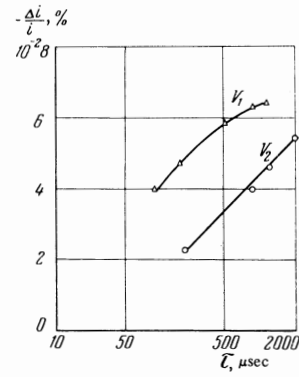


FIG. 8. Dependence of $\Delta i/i$ on pulse duration τ for different pulse amplitudes: $V_1 = 950$, $V_2 = 620$ volts. $H = 3000$ Oe, $l = 0.2$ cm.

properties. Traps are filled as the current increases; all traps are filled at a certain voltage V_t that depends on the trap concentration. For $V > V_t$ the current obeys the law $i \sim V^2$. In the presence of an infinite reservoir of carriers this law would be observed at all voltages $V > V_t$.^[9,10] However, in a liquid electrode the carrier concentration that can be injected into a crystal is finite (n_0). Therefore the maximum possible current is given by $i_m = n_0(\mu_+ + \mu_-)SVe/l$, where μ_+ and μ_- are the carrier mobilities and S is the electrode area.

Current-voltage curves exhibit two regions A and B, or three regions A, B, and C, respectively (Figs. 2 and 3), depending on whether the transition from $i \sim V^n$ to $i \sim V^2$ or the exhaustion of the electrodes occurs earlier. When a pulsed voltage is applied the space charge depends only on the number of free carriers. Therefore we have $i \sim V^2$ (Fig. 4). The linear region was ordinarily not reached, as a possible result of the fact that pulsed injection exhausts an electrode more slowly.

2. General character of the voltage dependence of L , $\Delta L/L$, and $\Delta i/i$. The interpretation of our results does not require that we begin with any hypotheses regarding the detailed mechanism of magnetic field influence on i and L besides the one that was justified in^[2-4]: the magnetic field influences the rate of carrier recombination.

We find that the electron and hole currents vary with depth in the sample (along the x coordinate) because of recombination in the bulk of the crystal. The current density is $j = j_+ + j_-$. From the continuity equation for holes, which is

$$\frac{dj_+}{dx} = -\frac{k}{eE^2\mu_+\mu_-}j_+(j - j_+) \quad (1)$$

with the condition $j_+ = \frac{1}{2}j$ at the center of the sample at $x = 0$ (where k is the carrier-recombination rate constant, E is the mean electric field in the sample, and μ_+ , μ_- are the carrier mobilities), we obtain

$$j_+ = j \left\{ 1 + \exp \left[\frac{kjx}{eE^2\mu_+\mu_-} \right] \right\}^{-1} \quad (2)$$

This solution was obtained neglecting space charge and assuming complete symmetry of electron and hole behavior.

The fraction of carriers that recombine during their passage through the crystal is given by

$$r = 1 - \frac{j_+(l/2)}{j_+(-l/2)} = \frac{e^{\alpha l} - e^{-\alpha l}}{1 + e^{\alpha l}} \quad (3)$$

where $\alpha = kj/2eE^2\mu_+\mu_-$ and l is the thickness of the sample. When $\alpha l \ll 1$ [which corresponds to $j/E^2 \ll (2-8) \times 10^{-13} \text{ a/cm}^2\text{V}^2$ as a function of l], we have $r = \alpha l$. When $kl \gg 1$ [corresponding to $j/E^2 \gg (2-8) \times 10^{-13} \text{ a/cm}^2\text{V}^2$], we have $r = 1$.

Since current variations in a magnetic field are associated with variations in the carrier recombination rate, we have $\Delta i/i \sim r$. For different segments of the current-voltage characteristic we obtain:

$$A (n > 2) \Delta i/i \sim E^{n-2} \text{ (Fig. 3),}$$

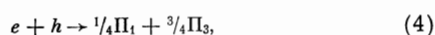
$$B (n = 2) \Delta i/i = \text{const (Fig. 3),}$$

$$C (n = 1) \Delta i/i \sim E^{-1} \text{ (Figs. 2 and 3).}$$

The fluorescence intensity resulting from carrier recombination is given by $L = Sjr$. We have $L \sim E^{2(n-1)}$, $L \sim E^2$, and $L = \text{const}$ for the regions A, B, and C, respectively. In a magnetic field $\Delta L/L \sim \Delta r/r = \text{const}$.³⁾

3. Magnetic-field dependence of fluorescence and current. a) It follows from^[2-4] that in anthracene the states which are "sensitive" to a magnetic field are large charge-exchange excitons, which we shall denote hereinafter by the Π . The changed lifetime of Π excitons in a magnetic field results from the mixing of the ψ functions representing para and ortho (with $m = 0$) exciton states. When these two magnetosensitive states are formed with equal probability, as in the case of the recombination of free electrons and holes, one-third of the long-lived ortho-excitons become short-lived as a result of mixing. We can expect that the reduced lifetime of Π excitons in a magnetic field will result in a smaller current through the sample if it is a true hypothesis that these excitons are generated through hole recombination and partial reverse dissociation.^[11] Confirmation of this expectation is found in the experimental results shown in Figs. 2 and 3.

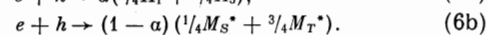
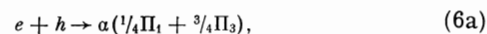
b) The Π excitons generated in carrier recombination can, as a general rule, induce both increased and decreased fluorescence intensity in magnetic fields. We know that the fluorescence observed as a result of hole-electron recombination represents the deexcitation of molecular singlet excitons.^[12] This result is found to be consistent with the formation of charge-transfer excitons if we assume, for example, that molecular excitons are formed from charge-transfer excitons:⁴⁾



where Π_1 and Π_3 are para- and ortho-excitons, M_S^* represents molecular singlet excitons, and M is the ground state of anthracene. The magnetic field mixing ortho- (with $m = 0$) and para- Π exciton states that are filled with equal probabilities will transform a fraction of the longer-lived Π_3 states into Π_1 states. However, in accordance with Eq. (5), this effect should lead to enhanced fluorescence. Since experiment has shown that L decreases in a magnetic field we must reject the scheme of successive exciton formation represented by (5).

c) A reduction of L when the rate of Π_1 generation is enhanced will result from the scheme described by the

following equations, where Π excitons and molecular excitons are formed in parallel processes:



Here α is the probability of Π exciton generation in the recombination event and M^* is a molecular triplet exciton.

According to (6) the diminished Π exciton lifetime leads to an enhanced rate of carrier recombination (in 6a), because a smaller fraction of Π excitons dissociate into carriers, and thus to reduced carrier concentration. At the same time the fluorescence caused only through process (6b) also diminishes.

The scheme represented by Eq. (6) accounts for the variation of i and L in a magnetic field and for the sign of $\Delta L/L$, but is hardly consistent with several other types of data. First, it follows from^[5,14] that the number of fluorescence quanta corresponds to the number of carriers recombining via process (6b) at $\alpha = 0$. At the same time the results obtained from the investigation of anthracene photoconductivity in a magnetic field require the occurrence mainly of process (6a) with $\alpha = 1$; otherwise one cannot account for the large negative photomagnetic effect observed experimentally (up to 12%).^[3,4,11] Secondly, with $\alpha > 0$ it is impossible to account for the fact that the delayed and fast fluorescence components are equal according to^[5] while $L_S/L_f = 0.6$ in our work. Considering that carriers are produced through the annihilation of molecular triplet excitons M_T^* ,^[4] it can easily be shown that according to the scheme of (6) this ratio becomes $L_S/L_f = 3(1 - \alpha)/(5 - 3\alpha)$ and disagrees with experiment when $\alpha = 0.2$ is reached. This scheme is therefore unsatisfactory.

d) When comparing the foregoing data obtained with the injection of carriers into anthracene and with their photoproduction, one must remember that molecular excitons M^* and charge-transfer excitons Π are generated via different processes: the recombination of injected electrons and holes in the first instance and the recombination of photoelectrons and holes in the second instance. It is reasonable to assume that the state of the recombining charges can determine which type of exciton will be generated.

By contrast with the case for carrier photoproduction, in the injection case a considerably longer time t elapses between the entrance of a carrier into the crystal and the recombination event. The time difference is associated with the fact that when carriers are photoproduced subject to a magnetic effect the density of electrons and holes in the region where they are generated by strongly absorbed light considerably exceeds their density in the double-injection case. In photoproduction the carrier density is such that a large fraction will recombine in a layer $\sim 10^{-4}$ cm thick. Under these conditions the magnetic field has maximal influence on the photocurrent;^[3,4] the layer in which injected carriers recombine is 0.1–0.2 cm thick. The ratio between the electron and hole concentrations in these two cases is estimated to be $\sim 10^2$.

When t is large, carriers can be trapped; then free and bound charges will recombine. The trapping of injected carriers is made evident by the steep dependence

³⁾The dependence of $\Delta L/L$ on E will be discussed in greater detail below.

⁴⁾This hypothesis was advanced in [13].

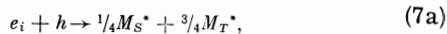
of i on V at low voltages. To determine the importance of trapping in connection with the magnetic effect, we injected pulsed currents into a crystal. For $\tau/T < 10^{-2}$ the peak values of i and L rose much more steeply than in the case of steady injection; this result provides evidence that the current was losing carriers through trapping (Fig. 4). However, in a magnetic field $\Delta L/L$ retained the same value as during continuous injection, thus providing evidence that the magnetic effect is not essentially affected by the presence of bound charges.

e) We shall now consider one additional difference between the recombination processes in the two cases being compared. When carriers are injected from electrodes containing positive and negative anthracene ions the crystal will contain charges localized on individual anthracene molecules (M^+ and M^-). In this case the carriers are tightly bound to the molecules and the electrical conductivity represents the motion of electrons in a narrow conduction band. It has been suggested frequently^[13,15,16] that anthracene also possesses a broad conduction band lying above the narrow band, with the separation of these two bands approximately equal to the affinity between electrons and anthracene molecules. Electrons in the broad band could possess greater mobility, but their lifetime would be limited by transitions to the narrow band (and by recombination processes). It appears that photoexcitation generates electrons in a broad conduction band. (It must be assumed that this generation occurs when molecular triplet ions are annihilated.^[4])

We shall assume that electron recombination in the broad and narrow bands leads to respectively different consequences. In the broad band electrons and holes can unite to produce a charge-exchange exciton (Π). These excitons are not generated in the narrow band, where recombination results in M^* excitation.

The conditions assumed here for the generation of large Π excitons are easily justified: The formation of a dynamical system consisting of a bound electron-hole pair requires a long mean free path and therefore high mobility that will enable an electron to revolve around a hole.^[17] These conditions are clearly not fulfilled if it is assumed that Π excitons are generated by electrons moving in the narrow conduction band (with mobility $\sim 0.5 \text{ cm}^2/\text{V-sec}$).

We thus advance the hypothesis that recombination involves the following processes of exciton generation:



Here e and e_i are electrons in the broad and narrow conduction bands, respectively.

The lowest exciton level Π_1 evidently lies below the molecular singlet exciton level M_S^* at 3.15 eV,^[12] so that the annihilation of Π_1 is radiationless. These relative locations of the Π_1 and M_S^* levels are supported both theoretically^[18] and by experimental data on the positive magnetic effect which indicate that the direct populating of the Π_1 state from M^* is possible.^[2,19]

Our present results indicate that the investigated fluorescence is sensitive to a magnetic field only when the crystal contains molecular triplet excitons (Figs. 5–7). Since it was previously shown that the annihilation of the triplets results in carrier generation,^[4]

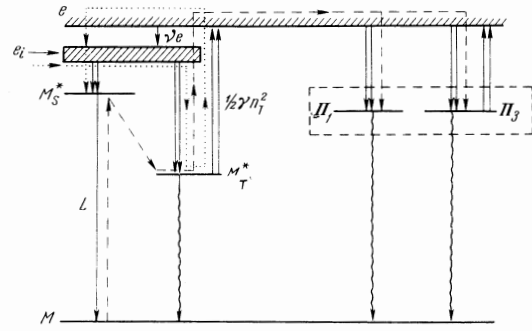


FIG. 9. Transition scheme in an anthracene crystal following double current injection or the photoproduction of molecular singlet excitons. The relative positions of the levels representing molecular excitons M^* and charge-transfer excitons Π are arbitrary. The dotted line designates the main path of carrier transformation and recombination in the case of injection. The dashed line designates the path of carrier generation and recombination in the case of crystal excitation by high intensity light. L designates fluorescence. The wavy lines designate radiationless transitions, and the paired arrows pertain to transitions in bimolecular processes.

carrier injection into the narrow band leads to electron generation in the broad band via the process



Therefore, the appearance of carriers in the broad conduction band and, consequently, the generation of "magnetosensitive" Π excitons constitutes, according to (7) and (8), a direct consequence of the presence of molecular triplet excitons.

Figure 9 illustrates the difference of the circumstances attending the generation of excitons and fluorescence by the two means of crystal excitation—carrier injection and very intense light—as represented in (7) and (8). The dotted and dashed lines designate the main paths of carrier generation and annihilation. In the first case recombination occurs mainly from the narrow conduction band, in the second case from the broad band. The ratio between the two paths of recombination clearly depends on the probabilities that electrons in the broad band will recombine with holes or will drop into the narrow band. Therefore this ratio depends on the crystal excitation density.

f) Our present results enable us, within the framework of the scheme represented by (7) and (8) (Fig. 9), to evaluate the rate of electron transitions from the broad to the narrow band. Let us consider a system of equations describing stationary concentrations of electrons and triplet excitons, averaged over a sample:

$$dn_i/dt = j^k/e - kn_i n_p - \beta n_i + \nu n = 0, \quad (9)$$

$$dn/dt = \frac{1}{2}\gamma n_T^2 - k_{\Pi} n n_p - (\nu + \beta') n = 0, \quad (10)$$

$$dn_T/dt = \frac{3}{4}k n_i n_p - k_{\Pi} n_T - \gamma n_T^2 = 0. \quad (11)$$

In (9)–(11), j^k is the electron current density at the cathode [$j^k = j^a = j/(2-r)$], n_i , n , and n_p are the electron concentrations in the narrow and broad bands and the hole concentration; k_{Π} is the effective rate constant of hole recombination with electrons in the wide zone, varying with the magnetic field; ν is the rate constant of $e \rightarrow e_i$ transitions; β and β' are the reciprocals of electron transit times in the narrow and broad bands;

k_1 is the rate constant of the radiationless annihilation of triplet excitons; n_T is the concentration of triplet excitons; γ is the rate constant of the bimolecular annihilation of triplet excitons.

For $k_{\Pi}n_p \ll \nu + \beta'$ the solutions (9)–(11) lead to

$$L = \frac{Sl}{4} kn_p n_p = \frac{S}{4} \frac{j-h}{e} \left[1 + \frac{3\nu}{8k_{\Pi}n_p + 5\nu + 8\beta'} \right]. \quad (12)$$

This expression holds for the complete recombination of injected carriers in the crystal bulk [$\frac{1}{2}kn_p \gg \beta$ in (9)], and occurs on segments of the current-voltage curves where $i \sim V^2$. Moreover, in deriving (12) it was assumed that enough triplets are generated to provide for their annihilation mainly via bimolecular processes.

In the case of low triplet concentration (when pulses with $\tau \ll 1/k_1$ are used or for low carrier concentrations in a sample) the fluorescence L possesses only a fast component, since the main triplet annihilation process is monomolecular. The fast fluorescence component is represented by the first term in (12). The second term describes delayed fluorescence, which attains its maximum intensity when all electrons generated through the recombination of M_T^* triplets and entering the broad band undergo a transition to the narrow band ($\nu \gg \beta'$ and $k_{\Pi}n_p$). It here follows from (12) that $L = L_f + L_S = 2Sj^k/5e$ and $\delta = L_S/L_f = 0.6$ in accordance with experiment. We note that this ratio agrees with the data in^[5], whose interpretation required the assumption of equal probabilities for the processes $M_T^* + M_T^* \rightarrow M_S^*$ and $M_T^* + M_T^* \rightarrow M_T^*$.

The effect of a magnetic field reduces to a change in k_{Π} . Hole-electron recombination in the broad band results in the generation of charge-transfer excitons, some of which again dissociate into carriers.⁵⁾ The probability of exciton dissociation is directly proportional to their lifetime; therefore, when $\tau_{\Pi_1} \ll \tau_{\Pi_3}$ excitons will dissociate. Since one-third of the Π_3 excitons become short-lived in a magnetic field, we have for the ratio of the effective recombination rate constants: $k_{\Pi}(H)/k_{\Pi}(0) = 2$. From (12) and the data shown in Fig. 5 we obtain

$$\frac{\Delta L}{L} = -0.025 = -\frac{3}{5} \frac{n_p \Delta k_{\Pi}}{\nu}. \quad (13)$$

The last equation can be used to evaluate ν by means of the experimental information shown in Fig. 4. Taking $k_{\Pi} = 10^{-6}$ cm/sec,^[5] $\Delta k_{\Pi} = k_{\Pi}$, and $n_p = (2 \pm 1) \times 10^{11}$ /cm³, we obtain $\nu = (4.8-2.4) \times 10^6$ /sec. In calculating ν we assumed equal hole and electron currents through the crystal; experiments with one-sided injection of carriers into anthracene have shown that the hole and electron currents are commensurable.

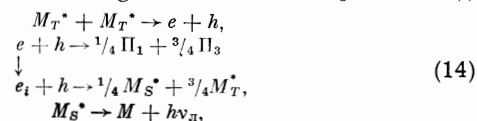
g) Enhanced voltage applied to the crystal in the region B ($i \sim V^2$) leads to enhanced carrier concentration and therefore to an increased rate of triplet generation along with delayed fluorescence. This result causes the steep rise of $\Delta L/L$ with V that is shown in Figs. 2 and 3. However, as V increases further, $\Delta L/L$ remains approximately constant; this result is consistent with the (neglected) fact that only the delayed fluorescence is

sensitive to a magnetic field, as was shown by the calculation in Sec. 2. The drop of $\Delta L/L$ at high V follows, according to the present scheme, from the fact that upper-band electrons reaching the electrode make transitions to the narrow band. For $\beta' \geq \nu$ the concentration of these electrons then decreases, thus reducing the relative role of recombination leading to Π exciton generation. Consequently the magnetic-field sensitivity of the fluorescence diminishes

CONCLUSION

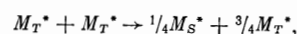
Our investigation shows that the scheme of (7) and (8) satisfactorily describes the overall experimental results and includes the generation of the molecular excitons responsible for fluorescence as a result of carrier recombination.

The scheme of the transitions (7) and (8) that is shown in Fig. 9 enables us to reinterpret certain experiments that were characterized essentially by the utilization of delayed anthracene fluorescence for the purpose of observing the concentration of molecular triplet excitons. These investigations had studied the diffusion of triplets in anthracene,^[20-24] had measured the probability of the $S \rightarrow T$ transition,^[12,25] and had studied the interaction of triplets with electrons.^[26] Since, in accordance with the discussion of our present results, delayed fluorescence arises through the following complex chain of processes: $h\nu + M \rightarrow M_S^* \rightarrow M_T^*$ (crystal excitation in the ground-state absorption band),



the intensity of this fluorescence depends essentially on the electron and hole concentrations. If their concentrations are high (for a high density of triplet generation), then when the lifetime of electrons e is shorter than $1/\nu \approx 10^{-6}$ sec, radiationless recombination of electrons and holes possesses higher probability.

In determining the M_T^* concentration from the delayed fluorescence density it is usually assumed that the only process occurring is



where there is no transient intermediate stage. This hypothesis entails a very large spread of the diffusion coefficients for the triplets, from 10^{-2} to 10^{-4} cm²/sec, which were calculated from experimental data without considering any transient and branched intermediate stage in the given process. Such a stage in the diffusion process can only reduce the measured diffusion coefficient. The minimum value of $D(M_T^*)$ must therefore be the preferred choice among all values given in the literature.

Calculations of the rate constant for the transition $S \rightarrow T(k_{ST})$ from the delayed fluorescence intensity also neglected the dependence of the delayed fluorescence yield on the crystal excitation density. We can account thereby for the surprising difference between two values of k_{ST} : 2.4×10^6 /sec in the case of excitation by weakly absorbed light^[25] and 3×10^5 /sec in the case of intense excitation.^[12] From the foregoing discussion it is seen that the minimum excitation density yields the more accurate (maximum) value $k_{ST} = 2 \times 10^6$ /sec.

⁵⁾ It has been shown in [11] that Π excitons dissociate into carriers via interactions between these excitons and molecular excitons.

- ¹E. L. Frankevich and E. I. Balabanov, *Fiz. Tverd. Tela* **8**, 855 (1966) [*Sov. Phys.-Solid State* **8**, 682 (1966)].
- ²E. L. Frankevich, *Zh. Eksp. Teor. Fiz.* **50**, 1226 (1966) [*Sov. Phys.-JETP* **23**, 814 (1966)].
- ³E. L. Frankevich and I. A. Sokolik, *Zh. Eksp. Teor. Fiz.* **52**, 1189 (1967) [*Sov. Phys.-JETP* **25**, 790 (1967)].
- ⁴E. L. Frankevich and I. A. Sokolik, *Fiz. Tverd. Tela* **9**, 1945 (1967) [*Sov. Phys.-Solid State* **9**, 1532 (1968)].
- ⁵W. Helfrich and W. G. Schneider, *J. Chem. Phys.* **44**, 2902 (1966).
- ⁶E. L. Frankevich and B. M. Rumyantsev, *ZhETF Pis. Red.* **6**, 553 (1967) [*JETP Lett.* **6**, 70 (1967)].
- ⁷P. Mark and W. Helfrich, *J. Appl. Phys.* **33**, 205 (1962).
- ⁸A. Rose, *Concepts in Conductivity and Allied Problems, Interscience*, New York, 1963 [Russ. transl., Mir, 1966, p. 87].
- ⁹R. H. Parmenter and W. Ruppel, *J. Appl. Phys.* **30**, 1548 (1959).
- ¹⁰M. A. Lampert, *Rept. Progr. Phys.* **27**, 329 (1964).
- ¹¹E. L. Frankevich and I. A. Sokolik, *Fiz. Tverd. Tela* **9**, No. 12 (1967) [*Sov. Phys.-Solid State* **9**, No. 12 (1968)].
- ¹²S. Singh, W. J. Jones, W. Siebrand, B. P. Stoicheff, and W. G. Schneider, *J. Chem. Phys.* **42**, 330 (1965).
- ¹³M. Pope and J. Burgos, *Mol. Cryst.* **1**, 395 (1966).
- ¹⁴W. Helfrich and W. G. Schneider, *Phys. Rev. Lett.* **14**, 229 (1965).
- ¹⁵J. J. Ewing and D. R. Kearns, *J. Chem. Phys.* **44**, 3139 (1966).
- ¹⁶M. Sano, M. Pope, and H. Kallmann, *J. Chem. Phys.* **43**, 2920 (1965).
- ¹⁷S. A. Rice and J. Jortner, *J. Chem. Phys.* **44**, 4470 (1966).
- ¹⁸V. A. Benderskiĭ, L. A. Blyumenfel'd, and D. A. Popov, *Zh. Strukt. Khim.* **7**, 370 (1966).
- ¹⁹E. L. Frankevich and E. I. Balabanov, *ZhETF Pis. Red.* **1**, No. 6, 33 (1965) [*JETP Lett.* **1**, 169 (1965)].
- ²⁰P. Avakian and R. E. Merrifield, *Phys. Rev. Lett.* **13**, 541 (1964).
- ²¹R. G. Kepler and A. C. Switendick, *Phys. Rev. Lett.* **15**, 56 (1965).
- ²²V. Ern, P. Avakian, and R. E. Merrifield, *Phys. Rev.* **148**, 862 (1966).
- ²³D. F. Williams, J. Adolph, and W. G. Schneider, *J. Chem. Phys.* **45**, 575 (1966).
- ²⁴M. Levin, J. Jortner, and A. Szöke, *J. Chem. Phys.* **45**, 1591 (1966).
- ²⁵S. Z. Weisz, A. B. Zahlan, M. Silver, and R. C. Jarnagin, *Phys. Rev. Lett.* **12**, 71 (1964).
- ²⁶W. Helfrich, *Phys. Rev. Lett.* **16**, 401 (1966).

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222